

THE APPLICATION OF INVERSE GAS CHROMATOGRAPHY TO COALS AND OXIDIZED COALS

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INTRODUCTION

In two previous papers (1,2) we reported preliminary results concerning the application of Inverse Gas Chromatography (IGC) to coals and air oxidized coals. In this paper we will report on the reproducibility of the IGC technique, its application to other Argonne Premium Coals, and compare the results with those obtained with pyrolysis mass spectroscopy. The objective of this study is to provide detailed information concerning the possible non-oxidative changes in the chemical and physical structures of the Argonne Premium Coal Samples (APCS) during long term storage. Inverse gas chromatography is just one of the techniques being utilized in meeting this objective. It is known that subtle changes in coal structure can effect changes in plasticity when a coal is heated. However, the techniques traditionally used to measure plasticity do not yield information which can be used to understand the underlying chemical and physical changes in the coal structure.

Inverse gas chromatography, a technique widely used for studying polymers, is being used to study the transitions that the APCS undergo upon heating. Inverse gas chromatography has been applied to polymers to measure the glass transition temperature, the degree of crystallinity, melting point, thermodynamics of solution, and chemical composition (3-5). Inverse gas chromatography has also been applied to coals in the temperature region less than 85°C to determine the enthalpy of sorption of methane and oxygen on dried coals (6). For methane the enthalpies of sorption ranged from 4.4 to 0.9 Kcal/mole for Czechoslovakian coals between 90.7 and 83.3 percent carbon on a dry ash free basis.

In contrast to classical gas chromatography, inverse chromatography probes the stationary phase, a coal, by determining the retention time of known compounds on it. This transposition of known and unknown in the gas chromatography experiment gives rise to the term "inverse chromatography". Two types of information are provided by the IGC experiment. The slope of a plot of the log of the retention time versus the inverse of the temperature is proportional to the enthalpy of retention for the probe molecule on the coal. This is a thermodynamic measure of strength of the interaction between the probe molecule and the coal. The temperatures at which major changes in slope are observed represent the points where the mechanism of retention has changed significantly, indicating that a significant change in the chemical or physical structure of the coal has occurred.

EXPERIMENTAL

The elemental compositions of the coals used in this study are shown in Table 1. The preparation of the Argonne Premium Coal Samples has been

described by K. Vorres and S. Janikowski (7). The -100 mesh samples were thoroughly mixed with non-porous glass beads (-400 to -60 mesh) to give a mixture approximately 10% coal on a weight basis. A blank experiment utilizing only glass beads yielded an effective slope of 0, indicating that adsorption of methane on the non-porous glass beads was minimal. The six foot by 1/4 inch glass columns were packed with ca. 30 grams of the mixture. All transfers and weighings were performed in a glove box under nitrogen atmosphere.

A diagram of the experimental apparatus is provided in Figure 1. The gas chromatography equipped with a single flame ionization detector could be controlled from an external computer. The injector was a computer controlled Carle gas sampling valve in a thermostated box. Flow control was provided by two flow controllers one with a 0-5 ml/min. element and the second with a 0-60 ml/min. element. The second controller was connected to the injector through a computer controlled solenoid. The experiment was controlled and the data analyzed by an IBM PC computer.

A flow diagram of the IGC experiment is shown in Figure 2. The experiment begins with an initial equilibration period of at least 24 hours, during which the flow rate of the helium carrier gas was cycled between it's chromatographic rate of 1 ml/min. and the higher rate (30 ml/min.). The higher flow rate was used to speed the removal of volatile matter from the column after each temperature increment. The probe, 10% methane in argon, was injected onto the column and it's retention time at the specific temperature determined. In the experiment duplicate chromatograms were obtained in four degree increments between 50 and 450°C. After each temperature increment the baseline signal was determined and compared to the baseline at the previous temperature. If it had increased more than 10% the solenoid isolating the second flow controller was opened increasing the rate at which the coal volatile matter was purged from the column. Even with increasing the flow rate, an IGC experiment could take up to a month to perform. The injector was held at 100°C and the detector at 400°C.

The Pyrolysis Mass Spectrometry (PyMS) technique has been described previously (8). Briefly the coal sample was placed on a platinum 5% rhodium mesh on the end of a probe as a slurry. After the solvent had evaporated the probe was inserted into the mass spectrometer and positioned within 5 mm. of the source. The probe which had been previously calibrated with an infrared thermometer was computer controlled to give a temperature profile beginning at 100°C and increasing at 50°C/min. to 800°C. This technique results in the relatively slow vacuum pyrolysis of the coal sample.

RESULTS AND DISCUSSION

The results from the IGC experiment on Upper Freeport Coal (APCS #1) are presented in Figure 3. The plot of the Log of the retention time versus the inverse of the temperature in degrees Kelvin is divided into three general regions based on the slope of the curve. The first major transition is bounded by the significant change in slope normally found between 100 and 120°C. We believe that this transition is caused by the loss of water from the pore structure of the coal. This change in slope indicates that the way the methane probe molecule interacts with the wet coal, or the mechanism of

retention, is different enough from that of the dry coal to produce the observed deviation in curve. The intermediate temperature region (ca. 115°C to ca. 350°C) is a long region in which a relatively constant slope is observed. This indicates that the mechanism of retention for the methane probe molecule does not change significantly. However, above 200°C a large number of small transitions are encountered which do not result in a major deviation from the prevailing slope. We believe that these are due to the loss of volatile matter occluded within the coal structure. The loss of relatively minor amounts of material should result in small deviations in retention time, which are observed but would not be expected to modify the overall mechanism of retention significantly. In region 3 (>350°C) there is a marked change in the slope indicating a major change in the mechanism by which the methane probe is retained by the coal in the IGC experiment. This corresponds to the temperature region in which Giesler Plastimeter results indicate that the coal is in the fluid state.

The reproducibility of the IGC technique is shown in Figure 4, where the results from duplicate experiments on Illinois No. 6 (APCS #3) are presented. As can easily be seen, the results from the two experiments are very similar. Not only do the major transitions occur at the same temperatures, but many of the minor transitions are reproduced as well. The two curves appear to be most dissimilar in the low temperature region. This is where we believe that changes in retention are dominated by water in the coal. Thus the results should be most sensitive to variation in sample handling. The minor transitions in the intermediate temperature region (120-300°C) are reproduced very accurately. Both curves show minor transitions around 190, 230 and 285°C. The temperature of the major transition appears to be similar for the two experiments. An exact assignment of the temperature of this transition in experiment two is impossible due to a problem with the data system, which resulted in the loss of data between 300 and 326°C. In the higher temperature region (>326) reproducible transitions occurred near 380 and 420°C. The enthalpies of sorption were very similar and well within the calculated precision of the data as can be seen in Table 2.

The variation in the temperature at which the major transition peak occurs for each of the coals studied are plotted versus percent carbon in Figure 5. This peak marks the start of the high temperature region in each of the experiments. This transition can be seen in Figure 3 just above 350°C for Upper Freeport coal, in Figure 4, just below 326°C for Illinois No. 6, and at 370°C in Pocahontas coal in Figure 7. The limited number of samples studied precludes stating that a correlation exists, however one is safe in assuming that a trend is indicated.

The enthalpy of sorption for each of the coals studied plotted versus carbon content is presented in Figure 6. The data was derived from the regression of the IGC data above the temperature of the major transition. As with the temperature of the major transition a trend is definitely indicated. However, several of the enthalpies are unrealistically high. This is probably due to changes in column void volume in this region which would significantly affect the calculated values.

Figure 7 compares the results from the IGC experiment with those obtained from PyMS for Pocahontas coal. Although the pyrolysis was started at 100°C, the total ion current signal below 208°C was dominated by an internal standard

added to the coal. Other experiments indicate that very little material of molecular mass >31 is released below this temperature. Above this temperature minor transitions in the IGC curve become more numerous. This indicates that these minor transitions in the IGC are indicative of the loss of volatile material. The maximum in the Total Ion Current (TIC) is observed at a temperature very close to that of the major transition in the IGC experiment. At temperatures above the major transition the TIC curve indicates that the release of volatile material begins to decrease significantly.

Overall, IGC appears to be a very reproducible method for following the chemical and physical changes that occur when coals are heated in an inert atmosphere. Differences in both the temperature of the transitions and enthalpies of sorption can be observed for coals of various rank. Pyrolysis Mass Spectrometry results indicate that the minor transitions observed in the intermediate temperature region are due to the loss of volatile matter from the coal.

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TABLE 1. Composition of Coals Studied.

Coal	% C (dmmf)	Empirical Formula
Upper Freeport mv Bituminous (APCS #1)	87.1	$C_{100}H_{75}N_{1.5}S_{0.3}O_{2.6}$
Illinois No. 6 hvC Bituminous (APCS #3)	77.8	$C_{100}H_{88}N_{0.6}S_{0.5}O_{3.7}$
Pocahontas 1v Bituminous (APCS #5)	89.6	$C_{100}H_{63}N_{1.2}S_{0.2}O_{3.3}$
Bruceton hvA Bituminous	82.3	$C_{100}H_{78}N_{1.6}S_{0.3}O_{9.3}$

TABLE 2. Enthalpies of Sorption in the Three Temperature Regions.

Coal	50-100°C	100-300°C	350-400°C
	Very Low Temperature Region†	Low Temperature Region†	High Temperature Region†
Upper Freeport mv	2.9 ± 0.5	$1.93 \pm .07$	12.5 ± 0.4
Pocahontas 1v	--- *	$2.01 \pm .04$	14.8 ± 0.4
Bruceton hvA	1.6 ± 0.2	$1.96 \pm .04$	7.7 ± 0.4
Illinois No. 6 (1)	4.0 ± 0.3	$2.00 \pm .16$	4.9 ± 0.5
Illinois No. 6 (2)	4.3 ± 0.3	$1.90 \pm .15$	5.1 ± 0.5

†Temperatures indicated are approximate, the actual boundaries were determined by the temperature of the actual transitions in the specific experiment.

*Pocahontas coal exhibited a negative slope in this region for some unknown reason.

Figure 1. Experimental apparatus for inverse gas chromatography experiment.

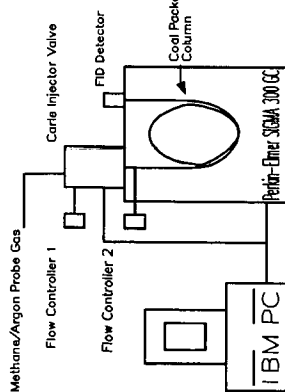


Figure 2. Flow Diagram of inverse gas chromatography Experiment.

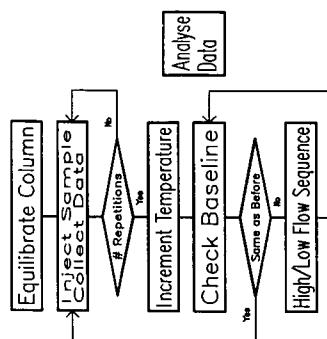


Figure 3. Plot of the log of the retention volume versus the inverse of temperature for Upper Freeport coal (APCS No. 1).

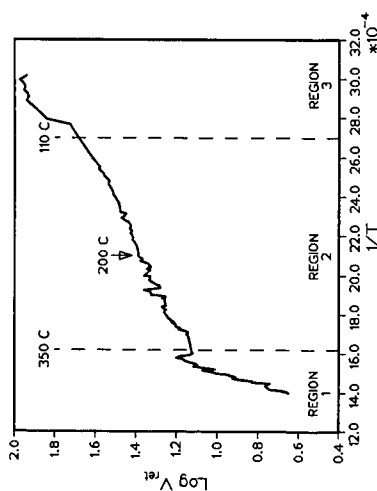


Figure 4. Comparison of IGC experiments on Illinois No. 6 coal (APCS No. 3).

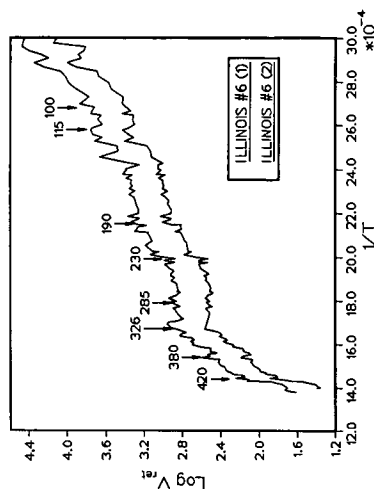


Figure 5. Variation in the temperature for the start of the major transition versus carbon content (dmmf) for APCs#3, Bruesdon, APCs#11, and APCs#5 coals.

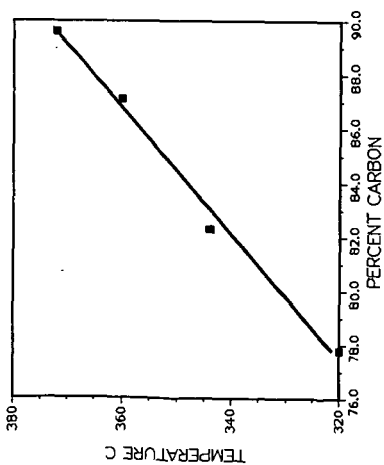


Figure 6. Variation in the enthalpy for the high temperature region (C50-450 °C) versus carbon content (dmmf) for APCs#3, Bruesdon, APCs#11, and APCs#5 coals.

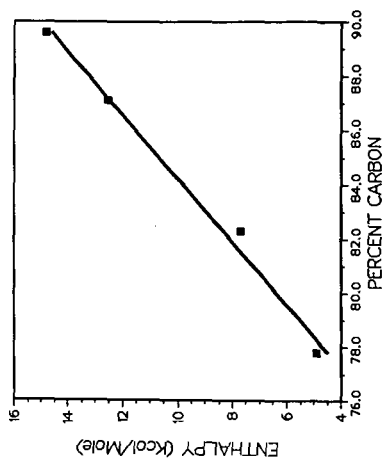


Figure 7. Comparison of IGC and pyrolysis high resolution mass spectrometry data for Pocahontas IV bituminous coal (APCS No. 5).

